Utility Patent Application

Title: Method and Apparatus for Preparing Nitride
Semiconductor Surfaces

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METHOD AND APPARATUS FOR PREPARING NITRIDE SEMICONDUCTOR SURFACES

SPECIFICATION

Statement of Government Support

Cross-Reference to Related Applications

Priority is claimed from U.S. provisional patent application Serial No. 60/213,149 filed

June 22, 2000 of R. Bruce Doak, Dirk C. Jordan and Christopher T. Burns. That application is

10   incorporated herein by reference.

Field of the Invention

This invention relates to the preparation of nitrogen containing films on substrates and

more particularly to preparation of nitride films on semiconductors by introducing nitrogen into a

15   corona discharge, thereby to produce activated nitrogen molecules for application to the

substrate.

Background of the Invention

Rapid progress has been realized in semiconductor technology related to the growth of group III metal-nitride films (III-N). Metal-organic vapor-phase epitaxy (MOVPE) has emerged as the leading "III-N" growth process, generally utilizing ammonia and trimethylmetallics as the precursors for nitrogen and group III metals, respectively. In contrast, and despite potential advantages over MOVPE, progress in molecular beam epitaxy (MBE) of III-N semiconductors has been slow. MBE offers a pristine UHV growth environment, a precise control over layer-by-layer composition, the ability to monitor growth *in situ* via standard surface science tools, and a wide choice of sources. For III-N growth, the latter include effusive or supersonic jets of MOVPE species, discharge sources of activated nitrogen gas, and evaporation sources of high purity metals.

AlN, GaN, and InN are emerging as materials of choice for wide band gap semiconductor devices. Despite the remarkable advances in III-N fabrication, further improvements of growth processes are needed.

Brief Summary

In accordance with this invention, certain electronically-excited (or "activated") nitrogen molecules are used as an ideal nitride precursor. This invention provides a method of producing $N_2A^3\Sigma_u^+$ in essentially a pure state as the sole excited species in a molecular beam whose only other component is ground state nitrogen. Through the use of this method, a high purity, high energy form of nitrogen is produced that when used in III-N fabrication, greatly improves upon both the quality and consistency of metal-III nitride and its production control. This method enables metal-III nitride film production to take advantage of the above discussed benefits of

MBE. (The terms "film" and "layer" are used interchangeably herein with no distinction intended.)

A corona discharge supersonic free-jet (CD-SFJ) source has been constructed, characterized, and operated to grow III-N nitride semiconductor films via molecular beam

5 epitaxy (MBE) using $A^3\Sigma_u^+N_2$, an electronically-excited metastable molecule. By "metastable" is meant molecules having a lifetime in their activated state sufficient to bring them to a location where nitride film growth occurs. The CD-SFJ yields $A^3\Sigma_u^+$ molecules as the sole activated species in a molecular beam otherwise containing only $X^1\Sigma_g^+$ ground state nitrogen molecules plus a negligible quantity of $^4S^0$ ground state nitrogen atoms. The generated beam has been used

10 as a nitrogen source to epitaxially grow metal-nitride (III-N) films via this rich content of excited metastable nitrogen molecules. Optical emission spectroscopy of the free-jet expansion reveals the expected cascade through the excited state manifold of N_2 triplet states to populate the $A^3\Sigma_u^+$ metastable state. Appearance potential spectroscopy (mass spectrometer detector ionization yield, measured as a function of electron impact energy) explicitly establishes the fraction of all

15 activated nitrogen species in the terminal beam, including non-emitting metastable species such as the $A^3\Sigma_u^+$ state. Metastable $A^3\Sigma_u^+$ molecules are present at up to 1.6% number fraction even several meters from the source, providing a beam intensity of 8.5×10^{16} metastables $sr^{-1}s^{-1}$. Growth studies confirm that $A^3\Sigma_u^+$ does incorporate very efficiently into a growing GaN thin film.

20 The electronically excited $A^3\Sigma_u^+$ nitrogen molecules couple to the ground state solely via the forbidden Vegard-Kaplan bands. The $A^3\Sigma_u^+$ lifetime is therefore very long, circa one second, and far greater than beam transit times through a molecular beam apparatus. Consequently, $A^3\Sigma_u^+$ molecules are metastable insofar as molecular beam chemistry is concerned, and can be

employed in molecular beam epitaxy (MBE) in the fashion of any stable beam species. The

suggested use of $N_2A^3\Sigma_u^+$ to grow GaN is based on two facts: (1) being an electronically excited

state, $A^3\Sigma_u^+$ is reactive ("activated"), and (2) being molecular rather than atomic, $A^3\Sigma_u^+$ delivers

two atoms simultaneously to the surface. Thereby, in a dissociative chemisorption reaction, one

5   of these two atoms can bind to the surface while the second carries away the heat of reaction as

kinetic energy. As a result, the strong exothermicity of the III-N reaction need not be dissipated

through the growing III-N film. Nitrogen accommodation is enhanced and sputtering damage

minimized, to yield high quality films at a growth rate limited only by the flux at which the

metastable molecules are supplied to the film.

10   Many different varieties of plasma sources, often incorporating supersonic jet techniques,

have been employed to "activate" nitrogen for III-N growth. These have included radio

frequency (RF) discharges, microwave discharges, electron cyclotron resonance (ECR)

discharges, various arc-jet discharges, and hollow anode plasma discharges. Invariably, these

sources produce a broad spectrum of both atomic and molecular excited states and often ionic

15   states as well. In marked contrast, a corona discharge supersonic free-jet expansion can yield

predominantly the long-lived metastable $N_2A^3\Sigma_u^+$ state and in appreciable quantities. As such it

becomes the primary candidate for testing GaN growth via $A^3\Sigma_u^+$ nitrogen molecules.

         The above and further objects and advantages of the invention will be better understood

with reference to the following Detailed Description taken in consideration with the

20   accompanying drawings.

Brief Description of the Drawings

         Fig. 1 is a diagrammatic illustration of a supersonic corona discharge source for use in

depositing activated nitrogen molecules on a substrate.

Fig. 2 is a fragmentary diagrammatic illustration of an alternative embodiment of the supersonic corona discharge source of Fig. 1.

Detailed Description

In Fig. 1, a corona discharge supersonic free-jet source 20 has a quartz tube 22 (6 mm

5   O.D., 4 mm I.D.), which has been heated and drawn to closure then ground back to form a nozzle orifice 23 with diameter of 200 μm as measured by an optical comparator. The tube 22 is mounted in a ¼" Swagelock cross 25 to allow as one electrode a tungsten or rhenium corona wire 26 (diameter 0.25 mm) to be inserted via a high voltage feedthrough 28 welded into the opposing leg of the cross. Source gas enters through one transverse leg 29 of the cross 25 as

10 indicated at 31. The opposing leg 33 serves as the means of mounting the cross on a ¼" stud 34, all within a source vacuum chamber 36. The nozzle was operated at a stagnation pressure of typically 200-440 Torr, producing a background pressure of 1×10^{-6} torr in the source vacuum chamber 36 pumped by an 18,000 1/s diffusion pump 37. A circular auxiliary electrode 38 was positioned just downstream of the nozzle, outside of the free-jet boundary, to provide a point of

15 attachment for the corona discharge. The discharge can be operated with the corona wire 26 either positive or negative with respect to the circular electrode 38. A current limited high voltage supply 39 to the corona wire was ballasted with a 250 kΩ 7 series resistor 41. Under these conditions a voltage of 4-6kV applied to the corona wire produces a discharge current of 6-18 mA and results in a readily discernible bright plume at the tip of the nozzle as

20 diagrammatically shown at 42. The turn-on procedure is as follows. The source gas is raised to the desired pressure. The current limit of the high voltage power supply to the corona wire 26 is set to the desired discharge current. The voltage is raised until the discharge initiated, whereupon the current jumps immediately to the current limit, placing the power supply in its

current-limited mode. Once the discharge is struck, the emission current can be adjusted within

bounds determined by the IV characteristics of the discharge.

A custom-made refractory graphite skimmer 40, with a diameter 0.75 mm opening 43 at

its apex, extracts the isentropic core of the free-jet plasma expansion to form a molecular beam.

5   Skimmers of the kind used here are described in D.C. Jordan, R. Barling and R.B. Doak,

Refractory Graphite Skimmers for Supersonic Free-jet, Supersonic Arc-jet, and Plasma

Discharge Applications, 70 Rev. Sci. Instrum. 1640 (1999), incorporated herein by reference,

and in U.S. provisional patent application Serial No. 60/092,815 of Jordan, Barling and Doak,

filed June 8, 1998, also incorporated herein by reference. The shape and the very sharp edge of

10   the front of the skimmer allow a shock wave to attach to the front of the skimmer. In this

aerodynamic flow configuration, the central portion of the beam passes into and through the

skimmer without being influenced by the skimmer edge. Further downstream of the skimmer,

where the beam density is much less, simple apertures in flat plates can be used as collimators

52--52_n for further collimation of the beam. Downstream of the skimmer, several differentially

15   pumped stages 44--44_n lead to a deposition chamber 46 where controlled growth can take place

under UHV molecular beam epitaxy (MBE) conditions.

The differential pumping is employed to ensure that essentially only the collimated,

directed beam provides reactants to the surface 49 of a target substrate 50 supported in a final

chamber 46 by a suitable means for locating the substrate as is diagrammatically indicated at 51.

20   Background gases in the various vacuum chambers 44--44_n also flow through a series of

collimators 52--52_n separating one chamber from the next. As mentioned, these may be simply

small openings in the wall separating one chamber from another or one or more may be a

skimmer similar to the skimmer 40. There occurs what is called "effusion" of the background

gas. Entering a chamber background gas is broadly distributed in angle (spread of about 100

deg) in contrast to the directed beam (about 0.5 deg). By using the several vacuum chambers 44-

-44$_n$ in series, with each separated from the next by a small collimator 52--52$_n$, this effusive flow

can be markedly reduced with no effect whatsoever on the directed beam. The collimators are

5   all carefully aligned in a straight line so that the directed beam, which is smaller in diameter than

the collimators, passes through them unhindered. This produces "differential pumping" to

reduce the background gas pressure and the background effusion from one differential pumping

stage to the next. The decrease in chamber pressures proceeding downstream from the source is

the desired result, but is not adjusted, per se, other than by setting the size of the apertures and

10   the size of the vacuum pump 54--54$_n$ in each differential pumping section. Depending on the

need in a particular application, greater or lesser elimination of effusion of the background gas

may be required requiring more or fewer of the stages 44--44$_n$. Typically, the pressure might be

0.0001 torr in the source chamber, 0.0000001 torr in the next chamber, and decrease by a factor

of 1/10 in each subsequent differential pumping section. All of these background pressures are

15   sufficiently low to result in no significant attenuation of the directed beam due to scattering from

the background gas molecules as the beam passes through each differential pumping chamber.

Photographs of typical corona discharge plumes are provided in Fig. 2 of the above-

identified provisional application Serial No. 60/213,149 that is incorporated by reference. The

appearance of the plume depended strongly on the polarity of the corona wire. The "positive"

20   corona discharge (i.e., the corona wire held positive with respect to the circular guard electrode)

ran at lower discharge current but somewhat higher voltage than the "negative" corona. The

positive corona developed a bright purple-violet plasma plume whereas the negative corona

plume was orange and less luminous. The positive corona was interrupted by continual

flickering and sparking while the negative discharge was steady and stable.

Apart from its very high initial gas temperature (several thousand degrees), a CD-SFJ is

similar to any supersonic free-jet. Its state specificity derives from rapid cooling within the free-

5   jet expansion. The corona discharge is struck within the nozzle tube, upstream of the nozzle

throat. As the gas expands through the throat into high vacuum, the rapid decrease in free-jet

density terminates the discharge within a few nozzle diameters of the throat. The expansion

itself, however, continues much farther downstream. This depopulates excited states, both by

collision-induced relaxation within the continuum portion of the expansion and by spontaneous

10   radiative relaxation in the free molecular flow regime further downstream. With proper selection

of discharge power, corona polarity, nozzle stagnation pressure, and nozzle diameter, all but

long-lived metastable species return to the ground state. The manifold of N_2 triplet excited states

cascades down to collect in the metastable $A^3\Sigma_u^+$ state, leaving only this plus the $N_2 X^1\Sigma_g^+$ ground

state in the terminal beam. "Skimming" and collimating the expansion forms a molecular beam

15   of these two species.

The relevant excited species in a CD-SFJ of molecular nitrogen are the N_2 triplet states

$A^3\Sigma_u^+$, $B^3\Pi_g$, $C^3\Pi_u$, and $W^3\Delta_u$. Other molecular excited states can also be present, as can

Rydberg states. Due to small excitation cross sections and/or short lifetimes, however, these

other states play no significant role. Electron impact excitation cross sections for the N_2 triplet

20   states are listed in Table I. Radiative lifetimes are presented for representative vibrational levels

of these species. The excitation cross sections peak at a fraction of 1 $\mathring{A}^2$ at electron impact

energies of 12-18 V.

Table I

Top two rows: Maximum integral cross sections for excitation of relevant N_2 species and electron impact voltage at which maximum occurs.
Following rows: Representative radiative lifetimes of species in various vibrational levels.

Excited Species	$A^3\Sigma_u^+$	$B^3\Pi_g$	$C^3\Pi_u$	$W^3\Delta_u$
Max. Excitation Cross Section	0.225 Å^2	0.299 Å^2	0.443 Å^2	0.380 Å^2
Electron Impact Voltage	17V	12 V	14 V	16 V
Radiative Lifetime, $\upsilon = 0$	1.3/2.5 s	8-13 µs	36-39 ns	4/32 s
Radiative Lifetime, $\upsilon = 1$	1.3 s	8-11 µs	36-39 ns	4.5 ms
Radiative Lifetime, $\upsilon = 2$	1.3 s	7-9 µs	37-38 ns	1.2 ms
Radiative Lifetime, $\upsilon = 3$	1.4 s	7-8 µs	38 ns	600 µs
Radiative Lifetime, $\upsilon = 4$	1.4 s	6-7 µs	36-39 ns	370 µs
Radiative Lifetime, $\upsilon = 8$	1.4 s	5 µs	---	130 µs

The terminal beam velocity for the current CD-SFJ pure N_2 was measured to be 2100 m/s under typical source settings. At this speed, and given the lifetimes of Table I, the $A^3\Sigma_u^+$ state will survive for kilometers and will clearly be present in the terminal beam. In contrast, $C^3\Pi_u$ will relax spontaneously within a few microns of its point of excitation. The $B^3\Pi_g$ state will

5   survive for only a few centimeters. The $W^3\Delta_u$ state might survive into the terminal beam. Re-excitation processes can alter these simple relaxation trends. The $W^3\Delta_u$ vibrational levels overlap with those of the $A^3\Sigma_u^+$ and $B^3\Pi_g$ and relax via a cascade through these latter states. This repopulates the $B^3\Pi_g$ states and gives rise to a long-lived afterglow on the $B \rightarrow A$ emission lines. Although this decay cascade is accelerated by collisions of excited N_2 with other beam species or

10   with background gases, the low vibrational levels of $W^3\Delta_u$ and (transiently) $B^3\Pi_g$ might still be present far downstream of the discharge.

The incorporated by reference provisional application Serial No. 60/213,149 reports on time-of-flight energy analysis, optical emission spectroscopy, and appearance potential spectroscopy for beams created by a CD-SFJ as described herein. Pitot (stagnation pressure

15   gauge) measurements of beam flux are there reported as are measurements of relative fractions of $N_2 A^3\Sigma_u^+$ excited state and $N_2 \, x \, {}^1\Sigma_g^+$ ground state in the terminal beam. Beams of 100% nitrogen as well as mixtures of 10% and 20% mole fraction N_2 in A_r are discussed there. Pitot measurements of absolute beam intensity are described, as are emission spectra from negative and positive CD-SFJ plumes. Both non-disassociative and disassociative ionization is

20   investigated by appearance potential spectroscopy and reported upon.

For the purposes of nitride layer growth, it is the flux of excited molecular species in the terminal beam which is significant. From the measured beam fractions of the excited states and with absolute pitot measurements of the terminal beam intensity, the appropriate excited state

fluxes at any desired working distance from the source are easily computed. Values are compiled in Table II for the 64 cm source-to-target distance of the current experimental configuration. Fluxes of a few tenth of one monolayer per second are readily achieved. As already apparent in Figs. 5a and 6a of the provisional patent application, Serial No. 60/213,149,

5   the beam fraction and therefore the flux of excited species increases significantly with increased discharge current. Optimum fluxes were obtained with a new graphite skimmer having the sharpest possible leading edge. Yet even upon averaging over 100 hours of operation, the average flux decreased by less than a factor of two from this optimum. This flux suffices for a growth rate of one to several hundred Angstrom per hour. This can be increased in one of

10   several ways as mentioned below. This rate is, nevertheless, sufficient for production of certain semiconductor substrate and nitride layer capable of use in a semiconductor device, including but not limited to ultrathin transistor gate dielectrics of high dielectric constant as discussed further below.

          CD-SFJ beams of argon/nitrogen mixtures also readily yielded the $N_2A^3\Sigma_u^+$ state. In fact,

15   with a negative corona discharge and 20% mole fraction mixture of nitrogen in argon, the flux of excited species was essentially the same as with 100% nitrogen gas. Since the nitrogen velocity in this dilute "seeded" beam is lower by roughly $(m_{Ar}/m_{N2})^{1/2}$, it follows that the absolute density of excited states must be even higher in the mixture than in the pure nitrogen beam. The metastable flux decreases at concentrations both higher and lower in nitrogen than the 20%

20   mixture. Measurements were made down to 10% nitrogen/argon mixture, below which there was insufficient intensity to record accurate APS curves.

          Using the CD-SFJ source of $N_2A^3\Sigma_u^+$, AlN and GaN films were grown on Si(100) and 6H-SiC(0001), Ga and Al being supplied from effusive sources indicated schematically at 56.

Table II

Flux of excited molecular nitrogen from CD-SFJ source as extracted
from appearance potential spectroscopy and pitot measurements. Two values
listed for 100% N_2 at 18 mA, corresponding to measurement with a
pristine skimmer (best achievable flux with current apparatus, first row) and
an average over 27 actual deposition runs totaling 110 hours (second row).

Gas	Polarity	Discharge Current (mA)	Excited Beam Fraction (%)	Beam Intensity (10^{18} #/sr/s)	Excited Species Flux (10^{13} #/cm^2/s)
100% N_2	Neg.	18 (best)	1.74	6.47	2.75
"	"	18 (avg)	1.68	4.30	1.67
"	"	14	0.88	6.66	1.43
"	"	11	0.80	6.04	1.18
"	"	8	0.61	5.75	0.85
"	Pos.	6	1.04	1.84	0.47
20% N_2/Ar	Neg.	18	4.96	1.20	1.45
60% N_2/Ar	"	18	2.71	1.48	0.98

GaN was also grown on AlN buffer layers deposited *in situ* on SiC. The highest incorporation efficiencies and best epitaxial interfaces were obtained with a metal/nitrogen flux ratio of approximately 1.25. Growth rates with the current CD-SFJ source were 70 to 120 Å per hour. Over 30 separate deposition runs of various duration and source settings were carried out to

5 produce films ranging in thickness from 300 to 900Å. The films were characterized *ex situ* by Rutherford backscattering spectrometry (RBS), scanning electron microscopy (SEM), electron channeling pattern (ECP), atomic force microcopy (AFM), and transmission electron microscopy (TEM). The measured incorporation efficiency (N atoms attaching per incident N_2 molecule) approached 100% and was independent of the substrate temperature from 600 to 900°C. A heat

10 (or cooling) source 61 may be incorporated as needed in the CD-SFJ to arrive at and maintain the desired temperature. Direct molecular chemisorption seems to be the underlying growth mechanism. Both hexagonal and cubic GaN films could be grown with an abrupt, well ordered epitaxial interface on 6H-SiC(0001) and with good crystallinity in the film. Good epitaxial interfaces were obtained even when GaN was grown directly on SiC.

15 The described corona discharge metastable nitride source can be used to apply a nitride layer to a multilayer substrate. For example, the substrate may comprise a semiconductor stratum, of for example Si or Se, and an epitaxial oxide layer on which the nitride layer may be grown.

The described corona discharge metastable nitrogen source can be used to grow silicon

20 oxynitride gate dielectrics. As in the growth of GaN and AlN epitaxial films, the dissociative reaction of the metastable nitrogen molecules will promote efficient local attachment of the nitrogen within the growing dielectric film, allowing growth of oxynitride films of any desired composition profile. This is important to current semiconductor devices, the further

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miniaturization of which will be limited in the very near future (ca. 2006) by the properties of the

silicon oxide gate dielectrics that are currently the industry standard.

The corona discharge free-jet source described produces an average $N_2A^3\Sigma_u^+$ metastable

intensity of 7×10^{16} metastables sr^{-1} s^{-1}, two orders of magnitude higher than intensities reported

5   for rare gas metastables. Growth studies verify that $N_2A^3\Sigma_u^+$ is a very efficient nitrogen reactant

for MBE growth of III-N semiconductor thin films. For commercial growth, an increase in

$N_2A^3\Sigma_u^+$ flux of at least one order of magnitude would be desirable. Similarity laws for glow

discharges suggest that this might be realized by simply decreasing the diameter of the CD-SFJ

nozzle and operating at higher nozzle stagnation pressure. Specifically, the concentration of

10   metastables produced in a single stage glow discharge excitation is predicted to change by a

factor of a^{-2} if the linear dimensions of the discharge are increased by a factor of a. To maintain

similarity under the new source dimensions, the stagnation pressure p of the discharge must be

changed by a factor of a^{-1}. Since the throughput of the supersonic nozzle scales as roughly $p\,d^2$,

the metastable concentration in the CD-SFJ is expected to scale as a^{-1}. If these similarity laws

15   apply, the metastable throughput will be increased by decreasing the linear dimensions of the

source and raising the nozzle pressure proportionally.

An extension, both for purposes of increased intensity and for beam uniformity, would be

to employ an array of miniature CD-SFJ nozzles and to skim with a very large diameter

skimmer. Glass capillary tubing is easily "pulled" to rupture at a neck diameter of under 1 μm

20   and miniature nozzle tubes fabricated in this fashion could be bundled to form a nozzle array.

Even smaller sized nozzle tubes have been formed in this laboratory by pulling hollow core

optical fibers (375 μm O.D. x 15 μm I.D.) and these have been demonstrated to yield high speed

ratio supersonic free-jets. In corona discharge applications, joule heating at a given discharge

current will ultimately set the minimum diameter of the corona wire and therefore the inner

diameter of the nozzle tube. Additional CD-SFJ intensity might also be obtained by terminating

the corona discharge not on an external guard anode, as in the current experiments, but on the

skimmer itself. This is diagrammatically illustrated in Fig. 2. Neuschäfer et al., at 117 Chem.

5   Phys. 133 (1987), incorporated herein by reference, report being able to achieve somewhat

higher intensities in this fashion, albeit at a cost in simplicity, dependability, and skimmer

lifetime.

    Although preferred embodiments of the invention have been described in detail, it will be

readily appreciated by those skilled in the art that further modifications, alterations and additions

10   to the embodiments disclosed may be made without departure from the spirited scope of the

invention.